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AND ORGANOMETALLIC COMPLEXES

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EXCITED-STATE PROTON TRANSFER KINETICS IN 1-NAPHTHOL COMPOUNDS
AND ORGANOMETALLIC COMPLEXES*

by

S. L. Shapiro, K. R. Winn, and J. H. Clark^{**}

ABSTRACT

We report direct measurements of excited-state proton transfer kinetic of 1-naphthol compounds + organometallic complexes: sample purity is essential.

* Work performed under the auspices of the U.S. Department of Energy.

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Excited-State Proton Transfer Kinetics in 1-naphthol Compounds and Organometallic Complexes

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Upon photoexcitation numerous aromatic hydroxy compounds undergo ultrafast proton transfer reactions in aqueous solution. Picosecond spectroscopy offers the opportunity of modelling proton transfer in solution by measuring the kinetic rates of similar aromatic derivatives as well as of a variety of compounds. Because upon absorption of light quanta aromatic molecules can become considerably more acidic due to the alteration of the electronic structure, the dissociation constant for proton ejection may change by many orders of magnitude.[1] For naphthol molecules in aqueous solution the proton transfer to the neighboring water molecules may be represented schematically as follows:

Fig.1 Simplified schematic of excited-state proton transfer in naphthol compounds. Also possible are nonradiative deactivations induced by interactions with protons.

where k_r and k_{nr} represent the radiative and nonradiative decay rates for the excited naphthol molecule (ROH^*), k_f is the deprotonation rate, k_b represents the backward protonation rate and ν and ν' are the emission frequencies from the protonated and deprotonated species, respectively. Forster [2] and Weller [3] have provided the essential theoretical ground work for proton transfer phenomena in the naphthol compounds. Because the naphthols become much more acidic upon excitation, it is possible to adjust the pH of the solution so that the only ground state species present is

ROH. Then upon excitation with a picosecond pulse, the protonation kinetics can be determined by observing the disappearance of ROH* at frequency ν or the appearance of RO* at the red shifted frequency ν' by means of a streak camera.

The dissociation of 1-naphthol occurs so rapidly that the fluorescence from the neutral form, ROH*, has been described as hardly noticeable.[4] Apparently nearly all of the fluorescence originates from the naphtholate ion. Here we report on the proton transfer characteristics of a series of 1-naphthol compounds and also report preliminary data on proton transfer in an organometallic complex of ruthenium.

Experimental Arrangement and Sample Preparation

Crucial to the success of the experiments and to their interpretation are the sample preparation and purity. All samples were obtained from LC Laboratories and were greater than 99.5% pure. Most importantly, all naphthol samples were purified and stored under oxygen-free conditions. Samples were prepared in a nitrogen box, and all solvents were thoroughly degassed by undergoing successive freeze-thaw cycles. As we shall see, these procedures were necessary.

The experimental arrangement for detecting the temporal fluorescence characteristics is shown in Fig. 2. A single 30 psec pulse is selected from

Fig.2 Experimental Arrangement for Measuring Rapid Proton Transfer

the pulse train of a Nd:YAG modelocked laser, is amplified, and can be frequency doubled, tripled or quadrupled with KDP crystals. The naphthols are excited with 266 nm radiation and the organometallics are excited with 355 nm radiation. Light emitted by the samples is collected onto the slit of a Hadland Photonics Photochron II streak camera. Streaks are imaged onto an OMA, and individual shots can be accumulated on a Nicolet 1074 signal averager by means of a precursor marker pulse. Fall times of the protonated species are obtained with a Corning 7-54 filter and risetimes of the deprotonated species with a Corning 2-62 filter.

Naphthol Compounds: Experimental Results and Discussion

The experimental results for the transfer rates in 1-naphthol and two of its derivatives are summarized in Fig.3.

Fig.3 Relaxation time for protonated species from 1-naphthol, 1-naphthol-2-sulfonate and 1-naphthol-5-sulfonate.

Note that 1-naphthol and two other 1-naphthol derivatives dissociate extremely rapidly. Kinetics of the rapid proton transfer indicate that the excited state pK value (pK^*) for all three derivatives is in the vicinity of zero. Notice also that the dissociation rate for 1-naphthol-2-sulfonate is slower than for the other two derivatives. Evidently, as one might have easily conjectured, an intramolecular hydrogen bond forms between the adjacent hydroxy and sulfonate groups, leading to a slowdown in the proton ejection rate in this derivative.

Our result in 1-naphthol-2-sulfonate differs strikingly from that of Zaitzev et al [5] who, using nanosecond techniques, reported that the dissociation rate for this compound is $5.4 \times 10^8 \text{ sec}^{-1}$ (1.85 ns). They also reported that degassing of their solutions had no effect upon the kinetics. However, as cannot be over emphasized, the difference between our measurement of 55 psec and other measurements indicating 1.85 ns can easily be proven to be connected with sample impurity. Our sample, prepared and stored under oxygen-free conditions, and dissolved in an oxygen-free solvent, yields a quite different result when exposed to air. Exposure of our 1-naphthol-2-sulfonate solutions to air produced an ≈ 2 ns component within seconds. Within a matter of minutes this longer component dominates the chronoscopy.

Similarly, a sample of 1-naphthol-2-sulfonate that was obtained from Eastman Kodak, where no attempt has been made to prevent exposure to air by the manufacturer and which contains possible contaminants as indicated by discoloration, yields only a long component in the temporal domain, also a few ns.

Exposure to air also affects the data from ultrapure 1-naphthol-5-sulfonate, where a long component also quickly develops. On the other hand, we have found that samples of 2-naphthol-6-sulfonate, reported upon previously, do not appear to be affected by air, judging from the kinetics.

For the case of 1-naphthol, Martynov et al. [6] estimated a dissociation rate of $> 3 \times 10^9 \text{ sec}^{-1}$. Our measurement of $25 \pm 10 \text{ ps}$ is in accord with their limit.

We also have observed a deactivation of the deprotonated species due to interaction with hydronium ions. The lifetime of the deprotonated species varies from nanoseconds to picoseconds with pH, and the values are in accord with the quantum efficiencies reported by Weller [3].

Previously, we suggested that by using intense laser pulses, the pH of a solution may be manipulated in an analogous fashion as the temperature in a T-jump experiment.[7] This might allow the study of rapid acid base reactions by a pH jump technique.[7,8] The rapid deprotonation of the 1-naphthol compounds demonstrates that the pH of a solution may be manipulated on a time scale of less than 20 ps. This rapid rate, the fastest intermolecular proton transfer process observed to date, offers the possibility of inducing very large and rapid pH jumps, for studying rapid chemical reactions.

Proton Transfer in an Organometallic Complex of Ruthenium

Figure 4 shows the schematic for the proton transfer reaction for the organometallic complex $(2,2' \text{ bipyridine})_2\text{Ru}(4,7\text{-dihydroxy-1,10 phenanthroline})$. The decay times for this fluorescence of the protonated and deprotonated forms of this complex in nondegassed solutions are also plotted as a function of pH. The protonated form decays in about 200 ns at pH 10. Previous studies by Bock et al [9] indicate that between pH 5 and pH 2.5, the protonated form will be the main species present in the

Fig.4 lifetime of protonated (triangles) and deprotonated (circles) species of an organometallic ruthenium complex.

ground state. Upon excitation between these pH values, we could then expect to observe a risetime corresponding to the formation of the deprotonated species. Because of the insensitivity of the streak camera at a wavelength of 800 nm, we have estimated that this risetime is less than 5 ns by using photomultiplier techniques. We are presently studying organometallic proton transfer processes from complexes that emit more toward the visible region.

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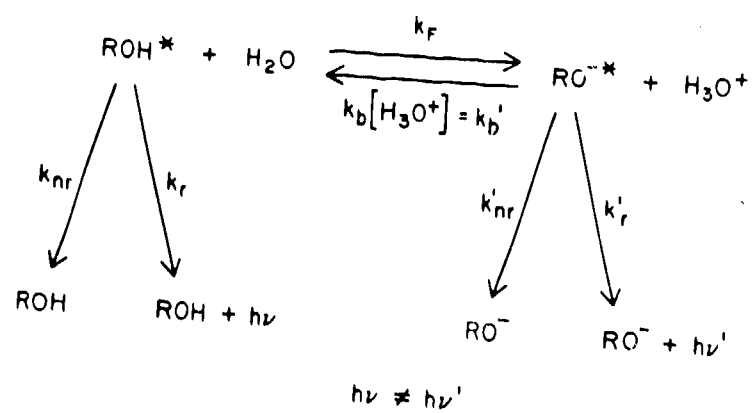


Fig. 1

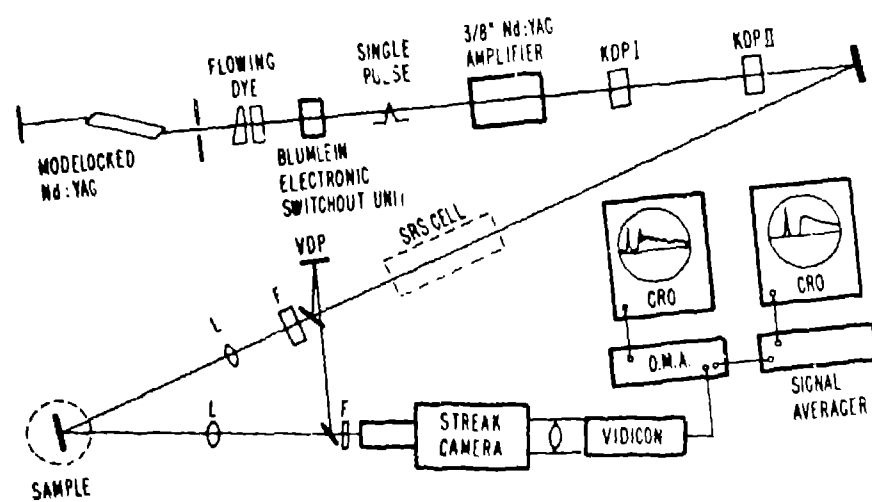


Fig. 2

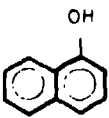
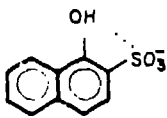
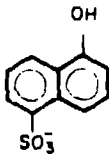
	1-naphthol	τ_D 25 ± 10 ps
	1-naphthol-2-sulfonate	55 ± 15 ps
	1-naphthol-5-sulfonate	≤ 20 ps

Fig.3

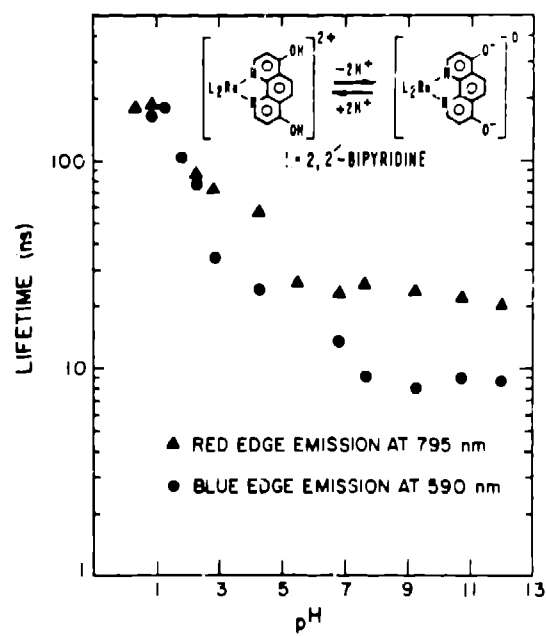


Fig. 4